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REGULAR ARTICLE

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Spin symmetry requirements in density functional theory: the proper way to predict magnetic coupling constants in molecules and solids

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Abstract In this paper it is argued that the use of density functional theory (DFT) to solve the exact, non-relativistic, many-electron problem, for magnetic systems requires imposing space and spin symmetry constraints exactly in the same way as it is currently done in ab initio wave function theory. This strong statement is supported on pertinent calculations for selected systems representative of organic diradicals, molecular magnets and antiferromagnetic solids. These calculations include several wave function methods of increasing accuracy and different forms of the exchange-correlation functional. The comparisons of numerical results carried out always within the same standard Gaussian Type Orbital atomic basis set show that imposing or not the spin and space constraints (restricted or unrestricted formalisms) leads to contradictory results. Therefore, it appears that, in the case of the Heisenberg magnetic constant, the present exchange-correlation functionals may provide reasonable numerical results although for the wrong physical reasons thus evidencing the failure of the current DFT methods to properly describe magnetic systems.

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1 Introduction

Magnetic systems imply the presence of unpaired electrons and may therefore appear equally in atoms, molecules or solids. For a large number of systems the magnetic moments are well localized on a given atom or group of atoms, referred to as magnetic centers; an effective magnetic moment, $\mathbf{S}_i$, can be associated to a given magnetic center i [1–3]. The physical description of magnetic coupling in a broad class of chemical compounds including organic biradicals, inorganic complexes and ionic solids is based on the use of the well-known phenomenological Heisenberg-Dirac-van Vleck Hamiltonian [1–5], which describes the isotropic interaction between localized magnetic moments $\mathbf{S}_i$ and $\mathbf{S}_j$ as

$$\hat{H}^{HDVV} = -\sum_{<i,j>} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where J_{ij} constant give the magnitude and type of interaction between $\mathbf{S}_i$ and $\mathbf{S}_j$ localized spin moments thus governing the energy difference between the different spin states arising from the interactions of $\mathbf{S}_i$ and $\mathbf{S}_j$. With this form of the spin Hamiltonian, a positive value of J_{ij} corresponds to a ferromagnetic interaction in which a situation with parallel spins is favored. The set $\{J_{ij}\}$ of parameters (their number and magnitude) defining this magnetic Hamiltonian characterizes the magnetic ordering of the system and permits one to describe the lowest part of the excitation spectra of magnetic systems. The sign and magnitude of the relevant (large enough) J_{ij} parameters result from the particular electronic structure that, at the same time, determines the stable crystal structure of the system. Hence, the magnetic order and the crystal structure of the system are consequences of the actual electronic distribution.

The understanding of magnetic interactions is essential to analyze and interpret, among others, neutron diffraction experiments and magnetic susceptibility measurements. Most important is the fact that magnetic interactions are at the hearth of molecular based magnets [1–6] or of High-T_c superconductivity [7] and largely dominate the chemistry of radicals [1,6,8]. Also, the description of magnetic states of damaged

DNA, RNA or protein oxidation adducts by radicals has an increasing interest because of their relevance to understand the biological activity of important carcinogenic and antitumor compounds. This is also important to investigate the structure, conformation dynamics and spectroscopic properties of these complex biological molecules [9–14].

From the discussion above, it is clear that for a complete picture of electronic structure, a detailed description of magnetic interactions is unavoidable. Rigorously speaking, this will require dealing with a fully relativistic formalism. However, the complexity of the *n*-electron relativistic problem does not permit to carry out the required calculations in the systems of interest. Still, one can use the non-relativistic Hamiltonian and handle magnetic interactions through a proper introduction of spin coordinates and spin symmetry. In this formalism, magnetic interactions in systems with localized magnetic moments result from important electron–electron correlation effects [1,8,15] which, to provide accurate theoretical estimates of J_{ij} values, must be appropriately described. This requires going beyond the usual mean field theories and therefore, the electronic structure of magnetic systems provide severe test cases for theoretical methods. In this respect, one must realize that the widely used density functional theory (DFT) based methods (For reviews on DFT methods, see for example Refs.) [16–25] is formally a mean field approach but in which all electron–electron correlation effects are taken into account through the exchange-correlation functional. Indeed, for the exact exchange-correlation functional one would get the exact solution of the non-relativistic *n*-electron Hamiltonian. However, since DFT does only make reference to the one electron density matrix, the treatment of open-shell systems is not straightforward although spin-polarized DFT is almost universally used [17–24]. Several authors have recently addressed the problem of using DFT to predict the singlet–triplet gap, or equivalent energy differences, in magnetic systems [4,5, 26,27]. The present work extends a previous analysis [28] and critically examines the reliability of magnetic coupling constants obtained by current implementations of DFT and show that the proper treatment of general open shell electronic states, where spin cannot be neglected, requires a revision of the current exchange-correlation potentials. This analysis is carried out by closely comparing the fundamental equations for the total energy of a given system as issued by wave function and density functional theory based approaches.

In this work, we consider the elementary non-relativistic many-electron problem and focus on the fundamental role of spin restrictions imposed to the exact wave function and to the corresponding reduced density matrices emphasizing its relationship to DFT (Sect. 2). This is followed by a detailed analysis of the problems encountered by DFT when applied to open shell systems and review of recent spin restricted formulations of DFT and, in particular, in the context of applications to obtain magnetic coupling constants (Sect. 3). Next, in Sect. 4, the relationship between spin restricted and spin unrestricted approaches in practical applications to solid state problems is discussed and important remarks are given. This is because the treatment of periodic systems necessarily relies on spin polarized description, which leads to conceptual difficulties in extracting the experimentally observable magnetic coupling parameters from the energy differences between magnetic states. This is certainly a problem for practical applications and also a matter of controversy. Moreover, the strong dependence of the results on the exchange-correlation functional as well as on the spin projection scheme considered put strong limitations on the capability of DFT calculations to provide reliable description of open shell systems. Section 5 provides strong evidence of this statement by accurate calculations on systems representative of organic biradicals, molecular magnets and antiferromagnetic solids. Finally, Sect. 6 presents the conclusions and further general remarks.

2 Remarks on wave function and density functional theory approaches

The exact solutions of the non-relativistic *n* electron problem are the different *n* electron $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$ wave functions satisfying the time independent Schrödinger equation which can be written as [29–35]

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{2}$$

For a system with *n* electrons and *N* nuclei and neglecting nuclear motion, the Hamiltonian of equation (2) becomes

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}, \tag{3}$$

with

$$\hat{T} = -\frac{1}{2}\sum_{i}^{n} = \nabla^2(i)$$

$$\hat{V}(\mathbf{R}, \mathbf{r}) = \sum_{i=1}^{n} v(\mathbf{r}_i) = \sum_{I=1}^{N}\sum_{i=1}^{n} \frac{-Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}$$

$$\hat{W} = \sum_{i>j=1}^{n} \frac{1}{r_{ij}}$$

where the first term stands for the electronic kinetic energy, the second term is the electron–nuclear attraction potential $v(\mathbf{r}_i)$ and $1/r_{ij}$ is the two electron interaction potential. The non-relativistic many-electron Hamiltonian (in the absence of magnetic fields) does not act on spin coordinates of the electrons. Nevertheless, anti-symmetry and spin restrictions are imposed on the wave function $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$ to satisfy the Pauli principle and spin symmetry requirements. This is the starting point for practical applications to the Hartree-Fock approach [36], Multi-reference Self Consistent Field approach [37,38], or Configuration Interaction approaches based on different selection/truncation of the CI series (See the general reviews [32–35] for details on all these methods).

Notice, however, that the spin restrictions are imposed on these wave functions not because they are approximate solutions of the Schrödinger equation. In fact, spin symmetry restrictions need to be imposed even on the Full Configuration Interaction wave function which is the exact solution of the Schrödinger equation in a finite subspace of Hilbert space. Neglecting this constraint would result in broken symmetry solutions where the total spin is no longer defined [39].

Defining γ_1 and γ_2, the usual one- and two- electron density matrices directly obtained from the $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$ wave function, as [29,31,32,40]

$$\gamma_1(\mathbf{r}_1; \mathbf{r}_1') = n \int \Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n) \times \Psi^*(\mathbf{r}_1' s_1; \ldots; \mathbf{r}_n s_n) ds_1 \ldots ds_n d\mathbf{r}_2 \ldots d\mathbf{r}_n \quad (4)$$

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \frac{n(n-1)}{2} \int \left\{\Psi(\mathbf{r}_1 s_1; \mathbf{r}_2 s_2; \ldots; \mathbf{r}_n s_n)\Psi^*(\mathbf{r}_1' s_1; \mathbf{r}_2' s_2; \ldots; \mathbf{r}_n s_n)\right\} \times ds_1 \ldots ds_n d\mathbf{r}_3 \ldots d\mathbf{r}_n, \quad (5)$$

the energy of the n-electron system in the field of N fixed nuclei can be written as

$$E = -\frac{1}{2} \int_{\mathbf{r}_1 = \mathbf{r}_1'} \left[\nabla . \nabla^T \gamma_1(\mathbf{r}_1; \mathbf{r}_1')\right] d\mathbf{r}_1 + \int V(\mathbf{R}, \mathbf{r}) \gamma_1(\mathbf{r}_1) d\mathbf{r}_1 + \int \frac{\gamma_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

where the quantities $\gamma_1(\mathbf{r}_1)$ and $\gamma_2(\mathbf{r}_1, \mathbf{r}_2)$ are the diagonal elements, $\gamma_1(\mathbf{r}_1) = \gamma_1(\mathbf{r}_1; \mathbf{r}_1)$ and $\gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$, of the spinless one- and two-electron density matrices (Eq. (4) and (5)), respectively [29,31,32,40]. Notice that the former is the one electron density $\rho(\mathbf{r})$ commonly used in electronic structure theory. Therefore, an accurate prediction of the energy of a given system in a given electronic state requires a reasonable estimate of $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$. It is customary to expand $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$ in a known basis set and to find the expansion coefficients using the variational method and with all necessary and sufficient constraints (spin and space symmetries) to prevent the variational collapse [41]; this is to avoid the convergence to a mathematical solution with no physical meaning. This is the basis of the so-called Full Configuration Interaction (*FCI*) method which provides the most accurate possible solution [40]. Indeed, for a finite basis set this is the exact solution and has extensively been used as a benchmark for quantum chemical methods [42–46].

Equation (6) is the starting point of DFT which aims to replace both $\gamma_1(\mathbf{r}_1; \mathbf{r}_1')$ and $\gamma_2(\mathbf{r}_1, \mathbf{r}_2)$ by the one-electron density, $\gamma_1(\mathbf{r}_1)$ or $\rho(\mathbf{r})$. For the ground state, this wish is brought up by the celebrated Hohenberg-Kohn theorems [47] which state that the exact ground state total energy of any many-electron system is given by a universal, unknown functional of the electron density only. Rigorously speaking, only the second term of the right hand side part of Eq. (6) is an explicit functional of the diagonal one-electron density matrix, $\gamma_1(\mathbf{r}_1)$. The first term, which corresponds to the kinetic energy is an explicit functional of the complete one-electron density matrix, $\gamma_1(\mathbf{r}_1; \mathbf{r}_1')$. The major contribution to the electron–electron term comes from the classical electrostatic 'self energy' of the charge distribution, which is also an explicit functional of the diagonal one-electron density matrix [29]. However, the remaining contribution of the electron–electron term is still unknown. This and the non-diagonal part of the electron kinetic energy term are usually added into a so-called 'exchange-correlation' functional which also depends on the one-electron density only ($E_{XC}[\rho]$). The definition of $E_{XC}[\rho]$ is the basis for the practical use of DFT. Since E_{XC} is a functional of the density it is possible to define a universal functional which is derivable from the one-electron density itself and without reference to the external potential $V(\mathbf{R}, \mathbf{r})$. Hence, DFT offers a way to eliminate the connection with the n-electron wave function working in terms of the density function $\rho_{\mathbf{r}}$ alone. In addition, since the first HK theorem states that there exists a one-to-one mapping between the external potential $V(\mathbf{R}, \mathbf{r})$ and the particle density $\gamma_1(\mathbf{r}_1)$ or $\rho(\mathbf{r})$, it follows that $\rho(\mathbf{r})$ determines the exact non-relativistic Hamiltonian [Eq. (2)] and hence one may incorrectly claim that $\rho(\mathbf{r})$ does also determine the ground state wave function $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$. However, one must admit that, even in the exact non-relativistic wave function, information regarding spin is introduced ad hoc to fulfill the Pauli exclusion principle and its consequent spin symmetry properties. In fact, the expectation value of the square of the total spin angular momentum ($\widehat{S}^2$), an experimental observable quantity, is univocally defined by $\gamma_2(\mathbf{r}_1; \mathbf{r}_2)$ but this will take physically meaningful values if and only if spin symmetry is imposed on the $\Psi(\mathbf{r}_1 s_1; \ldots; \mathbf{r}_n s_n)$ wave function.

Therefore, following McWeeny [29] one could reformulate DFT extending Levy's constrained search [48] to ensure not only that the variational procedure leads to a $\gamma_1(\mathbf{r})$ which derives from some wave function Ψ (the n-representability problem) but also that Ψ belongs to the totally antisymmetric irreducible representation (A) of the spin permutation group S_n (the Pauli principle). The above proposition can be written in a mathematical form by rewriting Eq. (6) as

$$E = \min_{\rho \to \gamma_1 \text{ derived from} \Psi \in A} \left\{ -\frac{1}{2} \int_{\mathbf{r}_1 = \mathbf{r}_1'} \left[\nabla . \nabla^T \gamma_1(\mathbf{r}_1; \mathbf{r}_1')\right] d\mathbf{r}_1 + \int V(\mathbf{R}, \mathbf{r}) \gamma_1(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int \frac{\gamma_1(\mathbf{r}_1)(1 - P_{12})\gamma_1(\mathbf{r}_2; \mathbf{r}_2')}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \right\} + \min_{\gamma_2 \text{ derived from } \Psi \in A} E_{\text{Correlation}}[\gamma_2(\mathbf{r}_1, \mathbf{r}_2)] \quad (7)$$

which clearly shows the one-to-one relation between the one-electron density, $\gamma_1(\mathbf{r}_1 \mathbf{r}_1')$, and the main part of the energy E and the explicit dependence of the electron–electron correlation on γ_2. According to the HK theorem, ultimately this part is also a function of the one electron density and hence one would have

$$E = \min_{\rho \text{ derived from } \Psi \in A} \left\{ -\frac{1}{2} \int \left[\nabla . \nabla^T \rho(\mathbf{r}) \right] d\mathbf{r} + \int V(\mathbf{R}, \mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho(\mathbf{r})] \right\} \quad (8)$$

where all unknown terms have been included in the exchange-correlation functional. Equation (8) recovers the constrained search as formulated by Levy [48] including explicitly the condition that ρ is derived from an antisymmetric wave function.

Notice that if $E_{\text{Correlation}}[\gamma_2(\mathbf{r}_1, \mathbf{r}_2)]$ in Eq. (7) is forced to be zero, one obtains another form of the well-known Hartree-Fock energy expression, whereas, if this is written in terms of the electron density as in Eq. (8) and ρ is indeed obtained from a single Slater determinant one obtains the Kohn-Sham (KS) equations [49]. This assumes that the non-diagonal terms of the kinetic energy and those arising from the permutation operator are all included in $E_{XC}[\rho]$. In the Hartree-Fock method, the energy is obtained through a variational iterative procedure which involves the non-local Fock operators [32] In the Kohn-Sham implementation of DFT [49], the variational problem possesses the same mathematical structure of the Hartree-Fock problem, it can also be solved iteratively leading to the well-known KS equations commented above. The current implementation of DFT based methods are almost universally based on the KS approach and only differ in the particular way to model the unknown $E_{XC}[\rho]$ term.

3 Density functional theory and the problem of open shells: spin restricted methods

The Kohn-Sham implementation of DFT for molecules with closed shell electronic structure and for non magnetic solids ensures that the Pauli principle is fulfilled and, at the same time, fixes the square of the total spin observable to zero. However, for open-shell systems the situation is by far less clear since by using only one Slater determinant, as in the spin polarized implementation of the Kohn-Sham procedure [50, 51], it may become impossible to satisfy the spin and spatial symmetry requirements. This is because only the S_z, the z component of the total spin, is defined, as in the case of spin polarized Hartree-Fock [52,53] (Unrestricted Hartree-Fock (UHF). The problem of computing atomic multiplet energies using DFT was analyzed in the pioneering work of Bagus and Bennet [54] extended later by Ziegler et al. [55] These authors already point out the difficulties of the Kohn-Sham formalism when applied to open-shell systems and provide some rules to compute the energy of a state with a defined value of $\widehat{S}^2$. A similar situation appears when using DFT to attempt to compute the singlet–triplet gap in an organic biradical or, equivalently, in a magnetic dinuclear complex with two unpaired electrons [4,5]. Unfortunately, the original works of Bagus and Bennet [54] and of Ziegler et al. [55] have not caused the large impact they deserve and, to a large extent, have been ignored by many theoretical chemists and physicists more worried to obtain a number close to the experiment than ensuring that the calculated value does indeed represent a physical state.

Nevertheless, the spin polarized Kohn-Sham formalism is broadly used to calculate the energy difference of the relevant magnetic spin states. In this case one has to rely on broken space and spin symmetry solutions to approximate [56,57] the low spin electronic states. This approach and its deficiencies have largely been described in previous works [4,5,26,27,58,59]. However, the use of a broken symmetry solution is still unavoidable for periodic systems. This point will be further discussed in the next section.

Recently, new DFT based methods have been suggested which aim to solve the problems encountered by spin polarized approaches. In these methods, one attempts to derive a spin-restricted formalism which would result in a proper description of open shell states; this is a description where $\widehat{S}^2$ is imposed and is hence well defined. This is precisely the common approach when using a wave function based electronic structure methods. DFT formalisms imposing $\widehat{S}^2$ are based either on spin restricted implementations of the Kohn-Sham equations [60,61] or on the time dependent DFT formalism applied to quantum chemical problems [60–62].

The time dependent DFT formalism may seem, at first sight, a good alternative to correctly describe magnetic systems within DFT and it is expected to provide reasonable values for energy differences between spin states. However, in the case of magnetic systems, the open shell nature of the low-spin state makes this approach unsuitable. This is because of the impossibility to construct a reference configuration which can produce both the singlet and the triplet states by single excitations only. In addition, the very small value of the energy differences between magnetic states ($\sim$10 meV or less) are well below the precision of current implementations of this method. Hence, even in a well-defined case, in which a subset of magnetic states could be described by single excitations on a given reference, the accuracy of this approach is still too poor. This is due to the important dependence of the energy values on the set of reference KS orbitals used to generate the excited electronic states. Therefore, one must conclude that time dependent DFT, in its standard form, cannot be used to calculate magnetic coupling parameters in magnetic systems.

The so-called spin-restricted open-shell KS (*ROKS*) and spin-restricted ensemble-referenced KS (REKS) formalisms proposed by Filatov and Shaik [63,64] furnish a general approach to treat low-spin open-shell states within the context of DFT and those are spin-restricted DFT methods considered in the present work. In the forthcoming discussion the REKS/ROKS methods will be presented in some detail and the basic equations compared to those of the general restricted-open shell Hartree-Fock method [36,38]. The REKS/ROKS approach is based on the ensemble representation for the density in DFT and combines it with certain ideas

from wave function theory for constructing the energy functional for ensemble densities. The non-interacting reference wave function within this approach is restricted to have definite values of both $\widehat{S}^2$ and $\hat{S}_z$ and therefore the constrained search in Eq. (8) including the spin coordinates is fulfilled. The energy and the density of a low-spin open-shell state (e.g. multiplet state with Γ and S space and spin symmetry, respectively) is represented as a weighted sum of energies (densities) of the contributing microstates, Φ_L, (see below)

$$E = \sum_L C_L E(\Phi_L) \tag{9}$$

and the corresponding density

$$\rho = \sum_L C_L \rho_L \tag{10}$$

with the 'weights' C_L restricted to sum up to unity.

$$\sum_L C_L = 1 \tag{11}$$

In turn, the microstates, Φ_L, are viewed as states of mixed symmetry (i.e. ensembles of pure states) which, in the non-interacting case, may be represented by single determinants, and their energies can be calculated within the standard KS approach [51]. Within the ROKS approach to multiplet states, the weighting factors C_L are fixed by symmetry, whereas in REKS they are obtained by minimizing the total energy

$$\begin{aligned} E_{\mathrm{ROKS/REKS}} = & \sum_{k\in\mathrm{Occ}} 2h_{kk} + \sum_{k,l\in\mathrm{Occ}} (2J_{kkll}) \\ & + \sum_{m\in\mathrm{Act}} f_m \left[2h_{mm} + \sum_{k\in\mathrm{Occ}} (2J_{kkmm}) \right] \\ & + \frac{1}{2} \sum_{m,n\in\mathrm{Act}} (a_{mm} J_{mmnn}) \\ & + \sum_L C_L E_{xc,L}(\rho_L^\alpha, \rho_L^\beta) \end{aligned} \tag{12}$$

where the C_L factors are variational parameters, h_{kk} and J_{kkll} are one and two electron integrals equivalent to those appearing in Hartree-Fock theory, $E_{xc}(\rho_L^\alpha, \rho_L^\beta)$ is the usual exchange-correlation energy which is calculated via the ρ_L^α and ρ_L^β electron densities for the microstate Φ_L. The vector coupling coefficients f_m and a_{mn} are related to the weighting factors C_L and to integer occupation number(s) of the spin-orbitals in microstate Φ_L as in Eqs. (13) and (14).

$$a_{mn} = \sum_L C_L (\eta_{mL}^\alpha + \eta_{mL}^\beta)(\eta_{nL}^\alpha + \eta_{nL}^\beta) \tag{13}$$

$$f_m = \frac{1}{2} \sum_L C_L (\eta_{mL}^\alpha + \eta_{mL}^\beta) \tag{14}$$

The microstates Φ_L are constructed from the set of KS orbitals (ϕ_k) which are obtained self-consistently with respect to the energy in Eq. (12). A detailed description of the orbital optimization techniques can be found elsewhere [63–65].

The use of ensemble representation leads to appearance of the fractional occupation numbers of the KS orbitals (ϕ_k) in the total density, i.e.

$$\rho = \sum_k n_k |\phi_k(r)|^2 \tag{15}$$

where

$$n_k = \sum_L C_L (\eta_{kL}^\alpha + \eta_{kL}^\beta) \tag{16}$$

The ROKS/REKS procedure shows important analogies with the restricted open shell Hartree-Fock method. Note, however, that, in the latter method, it is the wave function and not the energy and the density that is averaged over a set of microstates, which degenerate for the non-interacting electronic Hamiltonian. For multiplet states, the use of exchange-correlation functionals in ROKS/REKS provides better description of correlation stabilization effects [65]. Moreover, it is expected that the spin adapted description of ROKS/REKS approach should provide a correct description of the singlet–triplet splitting in diradicals or related systems which is free of the ambiguities arising from using spin unrestricted approaches based on broken-symmetry solutions [66,67].

A detailed comparison of REKS/ROKS equations with the general form of the restricted open-shell Hartree-Fock (ROHF) expression [38,68] for the expectation value of the electronic energy can be useful to understand some aspects of the method and to get insight into the approximations made. The general restricted open-shell Hartree-Fock equations can be written as follows [38]:

$$\begin{aligned} E_{\mathrm{ROHF}} = & \sum_{k\in\mathrm{Occ}} 2h_{kk} + \sum_{k,l\in\mathrm{Occ}} (2J_{kkll} - K_{kllk}) \\ & + \sum_{m\in\mathrm{Act}} f_m \left[2h_{mm} + \sum_{k\in\mathrm{Occ}} (2J_{kkmm} - K_{mkkm}) \right] \\ & + \frac{1}{2} \sum_{m,n\in\mathrm{Act}} (a_{mn} J_{mmnn} - b_{mn} K_{mnnm}) \end{aligned} \tag{17}$$

where K_{kllk} are the corresponding exchange integrals and

$$b_{mn} = \sum_L W_L^2 (\eta_{mL}^\alpha \eta_{nL}^\alpha + \eta_{nL}^\beta \eta_{mL}^\beta), \tag{18}$$

$$a_{mn} = \sum_L W_L^2 (\eta_{mL}^\alpha + \eta_{mL}^\beta)(\eta_{nL}^\alpha + \eta_{nL}^\beta), \tag{19}$$

$$f_m = \frac{1}{2} \sum_L W_L^2 (\eta_{mL}^\alpha + \eta_{mL}^\beta). \tag{20}$$

These coefficients, also known as state parameters, are fixed by the spatial and spin symmetry restrictions and a_{mn} and f_m are positive definite and evaluated using Eqs. (19) and (20), respectively. Note that the weighting factors W_L are used in the wave function averaging and thus they are squared in Eqs. (18–20). A more compact form of Eq. (17) is Eq. (21),

$$E = \sum_{m\in\mathrm{Occ}\cup\mathrm{Act}} f_m E_m \tag{21}$$

where f_m is evaluated according to Eq. (20). It is important to point out the close similarity between Eq. (21) and Eq. (9). However, in the case of REKS/ROKS, the dynamic correlation is included through the exchange correlation functional term which may be viewed as a modified two-electron integral or, equivalently, a "dressed" value of the matrix element of the Fock operator.

In order to conclude this discussion it is interesting to compare the ROKS/REKS and ROHF energy expressions above. One could argue that, for the case of two unpaired electrons, replacing the exchange correlation functional with the HF exchange the REKS description should be equal to that obtained with a complete active space self consistent field (CASSCF) calculation with an active space having two active electrons in two active orbitals [CASSCF(2,2)]. However, since CASSCF provides the best variational solution within the active space, the mixing of configurations minimizes both the dynamic and non-dynamic correlation energy, again within the given active space. The major difference between CASSCF and REKS concerns a possible double counting of the dynamic correlation. This is because the latter is a DFT method in which the dynamic correlation is supposed to be included via the correlation functional. Therefore, to avoid any double counting of dynamical correlation, the configuration mixing in REKS should minimize the non-dynamic correlation only, which leads to a certain difference in the results of REKS with the HF exchange and the results of CASSCF(2,2).

From the discussion above it also appears that the ROKS/REKS expressions are somehow related to average methods such as those proposed long ago by Nesbet [69] and McWeeny [32]. In more detail, the REKS energy functional with the HF exchange does not only reduce to the CASSCF(2,2) energy expression because, as a result of the different mixing coefficients, the REKS energy functional has a dependence on the occupation numbers of the active orbitals which is different from that of the CASSCF(2,2) wave functions. In fact, for two active orbitals $a = \phi_a$ and $b = \phi_b$, one has

$$E(\mathrm{REKS}) = \frac{n_a}{2}E(aa') + \frac{n_b}{2}E(bb') + (n_a n_b)^{3/4}\left[E(ab) - \frac{E(ab')}{2} - \frac{E(a'b)}{2}\right] \quad (22)$$

and

$$E(\mathrm{CAS}) = \frac{n_a}{2}E(aa') + \frac{n_b}{2}E(bb') + (n_a n_b)^{1/2}\left[E(ab) - \frac{E(ab')}{2} - \frac{E(a'b)}{2}\right], \quad (23)$$

respectively, where the primes indicate opposed spin and n_a and n_b are computed according to Eq. (16) for REKS and its corresponding version for CASSCF(2,2), respectively. These expressions become identical for $n_a = n_b = 1$, which is assumed to be the case of pure non-dynamic correlation, but slightly different otherwise. The REKS expression was intended to eliminate, as much as possible, the double counting of the dynamic correlation arising from the use of a reference system for the non-interacting electrons that effectively corresponds to a superposition of configurations. In the REKS method, the $(n_a n_b)^{3/4}$ prefactor in front of the coupling term in the energy expression in Eq. (22) comes from the geometric average between $(n_a n_b)^{1/2}$ and $(n_a n_b)$, which are the CASSCF and fractional occupation number DFT formalism proposed earlier by Slater [70] and revised more recently by Dunlap and Mei [71] and Averill and Painter [72]. Obviously, alternative options other than the geometric average can be defined by interpolating between the two limits. However, in general, the information needed to carry out such interpolation is insufficient.

4 Spin unrestricted density functional theory: implications for periodic calculations

Apart from the fundamental problem of the correct introduction of spin in DFT, this work is also motivated by the erratic DFT description of the non-dynamical electron correlation arising from configurational degeneracy [26]. For systems with two magnetic centers it has been shown that there exists a one to one mapping between spin eigenfunctions and the eigenstates of the Heisenberg Hamiltonian and also between the broken symmetry (BS) solutions obtained from *U*- formalisms and the eigenstates of the Ising Hamiltonian, respectively [1,4,5,56–58]. The former are eigenfunctions of S^2 whereas the latter are only eigenfuctions S_z. This mapping justifies the use of the Ising model and offers a consistent scheme to extract the magnetic coupling constants through the *BS* approach, either in the U-HF or U-KS schemes [4,5]. The mapping procedure leads to the same energy expressions suggested originally by Noodleman for the strongly localized limit [56,57]. In the case of U-HF, the mapping procedure does always lead to consistent results as discussed below for the molecular case. However, in the case of DFT it is customary to also use the mapping procedure or the corresponding spin projected solution [4,5,73,74]. The use of the unprojected results may obscure some important issues [4,5,28,56–58,75–77] and lead to some contradictions [5,28]. Still, the auxiliary nature of the KS orbitals makes this procedure at least controversial [4,5,78].

Electronic structure calculations for solid state systems face an additional difficulty. This is because periodic symmetry can be imposed rather easily to a single Slater determinant wave function or Kohn-Sham electronic reference system but so far have not been even formulated for multideterminantal wave functions. Therefore, solid state approaches to electronic structure are constrained to use spin polarized formulations. For the case of high spin coupling in the unit cell this choice does not pose additional problems. However, for the case of low spin or antiferromagnetic couplings this necessarily leads to broken symmetry solutions. This fact and the strongly correlated nature of many magnetic systems have resulted in strong limitations of current periodic solid state methodologies, either HF or DFT, to describe these fascinating solids. Only very recently the comparison between

Table 1 Singlet–triplet energy differences (J in cm^{-1}) in linear H–He–H for various H–He distances

Method		H–He distance		
WFN	Spin adapted	1.250 Å	1.6250 Å	2.000 Å
FCI	Yes	−4860	−544	−50
DDCI	Yes	−4815	−542	−53
CASSCF	Yes	−4250	−492	−50
CASCI	Yes	−3374	−415	−45
UHF	No	−1929	−213	−21
DFT				
B3-LYP	Yes	−5228	−624	−65
	No	−4196	−497	−55
B-PW91	Yes	−5871	−718	−75
	No	−4352	−452	−44
B-LYP	Yes	−6265	−792	−84
	No	−5138	−593	−65
PW91-PW91	Yes	−5778	−711	−74
	No	−4263	−441	−41
LDA	Yes	−7659	−1088	−124
	No	−6264	−776	−85

In the case of U- methods the BS–FM value has been considered. *WFN* and DFT methods are ordered according to their accuracy; for each family, the most accurate results first. For the DFT calculations, Yes stands for the REKS/ROKS results whereas No stands for the unprojected broken symmetry results

periodic U-HF with equivalent calculations on cluster models of the same systems have provided numerical arguments supporting the conclusion that the magnetic interactions are local in nature and that the same mapping procedure is needed to extract coherent J values [4,5,79]. It has been shown that the eigenstates of the Ising Hamiltonian provides, as in the case of molecular approaches, a general, coherent scheme to relate the energy difference between different magnetic solutions and J values. However, as pointed out above, one may argue that in the case of DFT approaches the use of the Ising model Hamiltonian and the corresponding mapping should not be used. Here, it is important to point out once again that the electron density does only define the non-relativistic Hamiltonian and, hence, spin properties need to be imposed. The comparison to cluster model calculations for the same system (whenever possible) within the same computational scheme and the use of the mapping approach provides so far the only possible guide.

5 Results and discussion on selected numerical examples

Selected magnetic systems has been explored with various definitions of the $E_{XC}[\rho]$ using either the approximate *BS* approach or the theoretically grounded REKS formalism. The choices for $E_{XC}[\rho]$ include the local density approximation (LDA) and several methods based either on the generalized gradient approach (PW91-PW91, B-PW91 and B-LYP) or on HF/DFT hybrid approaches (B3-LYP). For further details on the application of these DFT methods to magnetic coupling see also Refs. [4, 26, 27]. The accuracy of each approach is established by comparison to experiment and/or ab initio calculations using highly sophisticated wave function methods. The wave function methods chosen in the present study are complete active space configuration interaction (CASCI), complete active space self consistent field (CASSCF) and difference dedicated configuration interaction (DDCI) [80, 81]. These wave function based methods have been extensively used to describe magnetic coupling in a broad family of compounds and whenever experimental data is available the calculated results are all in the experimental range [79]. In all cases, the minimum *CAS* including the two unpaired electrons in two (magnetic) orbitals has been considered; the same active space is employed in the REKS calculations[1].

Results are presented for examples as representative of different families of systems with either ferro- or antiferromagnetic coupling. First, we consider the H-He-H model system for which the exact solution within a finite basis set is attainable. The second example is the 1,1',5,5'-tetramethyl-6,6'-dioxo-3,3'-biverdazyl radical; a prototype of organic diradicals. This is followed by the study of $[Cu_2Cl_6]^{2-}$ which can be considered an example of magnetic dinuclear transition metal compounds. Finally, results are presented for a cluster model representation La_2CuO_4. The latter is representative of High-T_c superconductor parent compound and also is used as an example of a system in condensed phase. These systems are especially well suited for this kind of study since they were also chosen to test the performance of multireference second order perturbation methods [82].

Tables 1 and 2 report the energy difference between the electronic states related to the magnetic order. The same standard Gaussian Type Orbital atomic basis sets are used for all methods[2]. For the R-formalisms, this energy difference corresponds to the singlet–triplet gap and, hence, it is directly

[1] CASSCF calculations through MOLCAS5.0 by Andersson et al., University of Lund, Sweden, 2003. CASCI and DDCI used the CASDI suite of programs by Maynau D and Ben Amor N, IRSAMC, Toulouse, 1997. The REKS and BS-DFT calculations through a modified version of GAUSSIAN98 (Rev. A.11) by Frisch et al., Gaussian Inc., Pittsburgh, PA, 1998; for REKS/ROKS implementation see Refs. [63–65].

[2] Basis sets: 6-31++G** for H and He; 6-3111+G for Cu; 6-31G* for C, N, Cl and O.

Table 2 Singlet–triplet energy differences (in cm^{-1}) for the biverdazyl radical, the $[Cu_2Cl_6]^{2-}$ and the two center cluster model representation of La_2CuO_4

Method		System		
WFN	Spin adapted	Biverdazyl	$[Cu_2Cl_6]^{2-}$	La_2CuO_4
Experiment	Yes	−769	[−40,0]	−1081±40
DDCI	Yes	−607	−7	−1129
CASSCF	Yes	−413	+13	−281
CASCI	Yes	−391	+17	−260
UHF	No	−314	+23	−152
DFT				
LDA	Yes	−1196	−99	−3665
	No	−920	−232	−3309
PW91-PW91	Yes	−933	+18	−2718
	No	−725	−169	−2438
B-PW91	Yes	−907	+18	−2701
	No	−709	−167	−2438
B-LYP	Yes	−942	+1	−2727
	No	−731	−177	−2445
B3-LYP	Yes	−479	+115	−895
	No	−605	−46	−954

In the case of U- methods the BS–FM value has been considered. WFN and DFT methods are ordered as in Table 1. Experimental results are discussed in Refs. [4,82]. For the DFT calculations, Yes stands for the REKS/ROKS results whereas No stands for the unprojected broken symmetry results

related to the Heisenberg J parameter. In the U-formalisms, the energy differences involve the ferromagnetic state ($|FM>$) and the space and spin symmetry broken solution ($|BS>$) which is generated via spin inversion on one center. In the particular case where Fock exchange is used and correlation neglected in $E_{XC}[\rho]$, it has been shown that $J = 2[E(|BS>) - E(|FM>)]$ since $|BS>$ is a 50% mixture of singlet and triplet states [4,56–59]. However, one can claim that, in the absence of magnetic fields, DFT is an effective one electron theory and consequently that S^2 and spin density are not rigorously defined in DFT and therefore one should not try to use the same concepts as in wave function theory [83]. The discussion on Sect. 3 has clearly shown that such line of reasoning is incorrect. Let us recall once again that the density determines the non-relativistic Hamiltonian and, consequently, spin properties have to be imposed as they are effectively imposed in wave function theory. Still, neglecting all these arguments one may, again incorrectly, claim that the DFT energy of the |BS> solution has to be taken as an approximation to the lowest singlet energy even if $\left\langle \hat{S}^2 \right\rangle$ and the spin-density are qualitatively incorrect [83]. In other words, one assumes that $J = E(|BS>) - E(|FM>)$. In what follows, it is demonstrated that the last supposition, although perhaps numerically acceptable [83,84] is in strong contradiction with the rigorous first principles discussed above. Furthermore, we will argue that this numerical coincidence with experiment is largely due to incomplete cancellation of the electron self-repulsion (contained in the classical Coulomb term of the KS Hamiltonian) by an approximate exchange functional $E_X[\rho]$ [84].

First, we comment on the results obtained using the highly accurate DDCI method (Tables 1 and 2). In all cases, the calculated J values are comparable to experimental available data and for H-He-H nicely reproduce the exact FCI values. The CASSCF and CASCI methods tend to systematically underestimate the superexchange contribution of J, because the dynamic electron–electron correlation effects are neglected [15,79]. In some cases, as in $[Cu_2Cl_6]^{2-}$, this lack of dynamical correlation leads even to qualitatively incorrect results [4]. The U-HF values (not shown) are close to CASCI or CASSCF results, provided that appropriate spin projection is carried out [4,5,54–59]. This is because the symmetry breaking introduces certain amount of non-dynamical electron-correlation [85,86], which is largely responsible for the superexchange contribution of the magnetic coupling parameter [15,79,87]. Here, it is important to remark that the U-HF projected J values are always consistent with the mapping procedure.

A totally different situation appears when examining the family of DFT results. The results summarized in Tables 1 and 2 show that REKS and U-KS results appear quite different and, in addition, the difference seems to be rather erratic and not following any general rule or definite trend. This is in a serious contradiction to the behavior of wave function based methods. In this case, *R-HF* (not shown) results largely overestimate the J value although the reason for such pathological behavior are well-known; it simply follows from the fact that R-HF calculations only include direct exchange and neglect all correlation, non-dynamical, and dynamical effects. However, spin projection is carried out provided U-HF calculations provide a fair estimate of the CASSCF results as indicated above. In the case of DFT calculations, the numerical results would suggest that in some cases one needs to carry out a pertinent spin projection whereas in other cases this seems unnecessary because of the fortuitous coincidence of R-KS and U-KS results. To make it worse, this erratic behavior is not only dependent on the particular choice of $E_{XC}[\rho]$ but it does also depend on the particular system

under study. The implications of these results are huge and indeed very serious because they indicate that, in absence of experimental references, DFT predictions of magnetic Heisenberg parameters obtained with the available approximate density functionals for $E_{XC}[\rho]$ cannot be trusted at all. At first sight, one can argue that the deficiencies of DFT methods are related to the "parametrization" of the particular approximate functional chosen to represent $E_{XC}[\rho]$. However, the strange behavior does also hold for LDA and GGA, which are derived from first principles for the uniform or weakly inhomogeneous electron gas, although the GGA implementations are only approximate. Results in Table 2 show that large differences between R-KS and U-KS values are found for the Cu binuclear complex (as one would expect by comparison to the HF theory). However, these differences are largely reduced for the biverdazyl organic radical and almost disappear for the La_2CuO_4 cluster model. This complete set of numerical results show how dangerous it is to make predictions on the magnetic coupling of biradicals, dinuclear systems, or magnetic solids. When the experimental result is known, one can investigate the performance of a given exchange-correlation potential in the usual U-KS implementation and decide whether from a pragmatically point of view it is better to project the result or not. This strategy may be useful in analyzing trends in a family of analogous compounds. However, when experimental results are not available, it is very difficult to decide the numerical recipe to be followed. This leads one to conclude that even if U-KS may predict a reasonable numerical estimate of the magnetic coupling parameter, which in turn can be in agreement with experiment, it is well possible that such a result is not justified from a rigorous application of theory.

From the above discussion one may reach the conclusion that the failure of current DFT methods to properly describe magnetic systems lies on the approximate nature of the exchange-correlation functional and argue that with the exact-correlation functional and with the appropriate spin constraints as in the REKS method one would necessarily get the exact value. This statement can be checked indirectly by making use of the well-known feature of DFT to reduce to the HF theory upon replacing its exchange-correlation functional with the Fock exchange only. This is true for the closed-shell KS theory, the spin-unrestricted KS theory, and the ROKS method, which reduces to the respective spin-restricted open-shell SCF theory of Roothaan [36], of course for those terms which can be described within the latter theory. However, this does not hold for the REKS method, which, upon replacing the DFT exchange-correlation with the HF exchange, does not reduce to the respective SCF theory, CASSCF(2,2). The major difficulty in combining the multi-reference approaches with DFT is that the double counting of the correlation energy (once via density functional and twice via configuration mixing) must be avoided. The MCSCF procedure describes both the non-dynamic and the dynamic correlation energy within a given active space. Following Savin et al. [88], one can subtract from the correlation functional that fraction of the dynamic correlation energy, which has been already included via the MCSCF procedure. Alternatively, one can eliminate the dynamic correlation from the MCSCF part. It is this latter route that is followed in REKS. Of course, there is no rigorous means to distinguish between the dynamic and non-dynamic correlation in molecules. Therefore, the REKS description of non-dynamic correlation only is an approximate model, which can be more or less precise. However, as shows Table 3, where the results of the DFT calculations carried out with the Fock exchange only are collected, the REKS (HF) description may not be entirely unreasonable. The REKS single–triplet differences are underestimated as compared to the CASCI or CASSCF ones, which suggest that at least a part of the dynamic correlation is correctly removed. Quite interestingly, the REKS energy differences are close to those obtained within the symmetry-broken UHF theory but without taking spin projection into account. One must remind that according to rigorous mapping procedures the energy difference between BS and HS is not the singlet–triplet gap but just half of its value. However, the numerical coincidence between the REKS/ROKS singlet–triplet gap and the corresponding value obtained through the broken symmetry approach (but without projection) when using HF exchange only may be simply accidental, because the broken-symmetry UHF theory describes incorrectly [85] both parts of the correlation energy, dynamic and non-dynamic.

6 Conclusions

The reported results provide compelling evidence of inconsistencies in the current implementations of DFT for open shell systems. In the case of U-KS formalism, the theoretical discussion in Sects. 2 and 3 shows unambiguously that the use of the projection procedure is strictly necessary to rigorously relate the calculated energies to energy differences between pure spin states. This is in agreement with the earlier suggestions of Bennet and Bagus [54] and Ziegler et al. [55] and is contrary to the claims of Perdew et al. [83] Hence, for the case of two unpaired electrons the singlet–triplet gap must be obtained as twice the difference between the energy of the broken symmetry solution and that of the highest spin setting. Accordingly, differences with respect to the experiment cannot be attributed to the treatment of the spin but to limitations of the exchange-correlation functional.

In the case of spin restricted implementations of DFT such as the REKS/ROKS methods used in this work, the numerical results again evidence inconsistencies of the current forms of the $E_{XC}[\rho]$. In fact, REKS/ROKS calculated values of the magnetic coupling constant are found to exhibit an erratic behavior with respect to experiment and wave function based methods. In some cases, the calculated REKS/ROKS values resemble the unprojected U-KS values, whereas, in other situations, they are quite far away from it. Moreover, this strange trend is not only system dependent but also functional dependent. Finally, we note that the REKS method does not reduce to the corresponding CASSCF(2,2) result when the HF-null functional is used.

Table 3 Singlet–triplet energy differences (J in cm^{-1}) in linear H–He–H for various H–He distances, the biverdazyl radical, the $[Cu_2Cl_6]^{2-}$ and the two center cluster model representation of La_2CuO_4

Method	H-He distance		
WFN	1.250 Å	1.6250 Å	2.000 Å
CASSCF	−4250	−492	−50
CASCI	−3374	−415	−45
UHF	−1929	−213	−21
DFT			
REKS/ROKS (HF-null)	−2533	−267	−25
Method		System	
WFN	biverdazyl	$[Cu_2Cl_6]^{2-}$	La_2CuO_4
CASSCF	−413	+13	−281
CASCI	−391	+17	−260
UHF	−314	+23	−152
DFT			
REKS/ROKS (HF-null)	−260	+19	−156

In the case of U- methods the BS–FM value has been considered. WFN and DFT methods are ordered according to their accuracy; for each family, the most accurate results first

Therefore, one must conclude that, although some meaningful trends regarding magnetostructural relationships arise from DFT calculations, comparing DFT values of the magnetic coupling constants to experiment is very delicate. In the case of U-KS methods one may obtain good numerical result but the price to be paid is to disregard fundamental constraints and sometimes even to completely lose the physical reference. However, the difference between taking or not into account the corresponding spin projection, a factor of 2 in the cases with one magnetic electron per center, decreases with increasing the number of unpaired spins; the factor is 1.50 for two electrons per center as in NiO and related systems and goes down to 1.25 for the case of Mn^{2+} compounds such as MnO. Therefore, in these cases the pragmatic advantage of the unprojected formula is lost.

In the case of the R-KS method the results are too system and functional dependent thus evidencing weaknesses in the current exchange-correlation functionals. In this respect, there is a need for a continued search of more accurate expressions of the exchange-correlation functional. There is also a need for new methodological developments that ensure that the calculated densities correspond to systems with a perfectly defined multiplicity. These new methods must fill in the existing gap between wave function and DFT approaches in what concerns spin properties. In this sense, the REKS/ROKS implementation of DFT is a first promising step since it avoids the formal problems of the unrestricted approaches and provides a proper representation of the electronic structure of atoms, molecules, and solids in the non-relativistic domain as in many-electron wave function theory. However, there is still place for improvement, in particular, with regard to the description of non-dynamic correlation only within the REKS method when the HF-null functional is used.

In conclusion, in order to use DFT to solve the exact, non relativistic, many-electron problem, one should impose the space and spin symmetry constraints as it is currently done in ab initio wave function theory. Bypassing this fundamental theoretical requirement would lead to inconsistent results. In the case of magnetic coupling, DFT can provide seemingly accurate numerical results but for the wrong physical reasons.

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